DOI: 10.1039/b101523k

IR spectroscopic study of NO and CO adsorptions on nonstoichiometric nickel–copper manganites

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The adsorptions and co-adsorption of nitric oxide and carbon monoxide on nonstoichiometric nickel and nickel–copper manganites have been investigated *in situ* by transmission infrared spectroscopy. Time-dependent and temperature-dependent data have been acquired to investigate the nature of the molecule–surface interactions. The surface chemistry of NO was found to be particularly rich, involving numerous surface species (mononitrosyls, dinitrosyls, adsorbed N_2O, nitrites/nitrates), whereas that of CO was somewhat simpler. The competitive adsorption of NO and CO was evidenced. However, with time, NO tended in all cases to colonize the surface of the samples, and Cu^+ cations were shown to be the only access points of CO to the surface of such oxides in the presence of NO. Finally, a time sequence of reactions was shown in the case of NO adsorption.

1 Introduction

Recent studies have shown that spinel materials such as nonstoichiometric nickel–copper manganites present interesting catalytic properties for the reduction of nitric oxide by carbon monoxide[1] at low temperature and short contact time (0.015 g s cm^{-3}). These oxides are finely divided (specific surface area in the range 150–250 m^2 g^{-1}) and cation deficient materials. This nonstoichiometry arises from the presence in the spinel structure of cations with oxidation states higher than in stoichiometric oxides and the overall electrical neutrality of the crystal is achieved by the presence of cationic vacancies.

The understanding of the mechanism involved in the CO–NO reaction can only be attained through a comprehensive approach of the chemical interactions existing between NO and CO molecules and the surface of these oxides. Chemisorption[2] and temperature programmed desorption[3] experiments have already been carried out, showing that, at room temperature, nitric oxide adsorbed on such oxides molecularly (not a dissociative process) and that NO was able to displace the majority of CO-preadsorbed molecules. However, carbon monoxide was found to possess a few specific adsorption sites on the surface.

The objective of the present paper is to report an *in situ* infrared spectroscopic study of the surface species formed upon adsorption of nitric oxide and carbon monoxide molecules (in static and flowing conditions) on nonstoichiometric nickel and nickel–copper manganites.

2 Experimental

2.1 Sample preparation

The nonstoichiometric nickel–copper manganites $Ni_xCu_yMn_{(3-x-y)}\square_{3\delta/4}O_{4+\delta}$ used here were synthesised by thermal decomposition, in air at 350 °C for 6 h, of mixed nickel–copper–manganese oxalates precipitated at room temperature in aqueous medium (see ref. 4 for additional details).

2.2 Infrared spectroscopy

The oxide samples ($m = 90$ mg) were pressed into 20 mm diameter wafers (thickness: 0.15 mm) and placed in a stainless steel cell (Harrick, 45 mm total path length of the IR beam) connected to a conventional vacuum/gas handling system. The sample could be cooled or heated between −20 °C and +350 °C. Before each adsorption experiment, the sample was outgassed under secondary vacuum (10 Pa) at 300 °C for 1 h. The experiments performed in static conditions were carried out by introducing a required pressure in the cell. For the experiments run in flowing conditions (at atmospheric pressure), a gas flow of 60 cm^3 min^{-1} was used with the gas compositions: 1% NO/Ar, 1% CO/Ar, 1% NO + 1% CO/Ar or 100% O_2. Transmission infrared spectra were recorded using a NICOLET 510P FT-IR spectrometer (MCT detector) in the 400–4800 cm^{-1} wavenumber region with a resolution of 4 cm^{-1}.

3 Results

Three types of static adsorption experiments were carried out on an outgassed surface of the samples: (1) adsorption of NO (1% NO in Ar); (2) adsorption of CO (1% CO in Ar); (3) adsorption of a stoichiometric mixture of NO + CO (1% NO + 1% CO in Ar).

To investigate the competitive adsorption behaviour of NO and CO, we have also carried out the adsorption of NO on a CO-preadsorbed surface and the symmetrical experiment: the adsorption of CO on a NO-preadsorbed surface.

Since the main goal of this study is the understanding of the CO–NO reaction mechanism, the above static adsorptions have been completed by experiments under the flowing gas mixtures: 1% NO in Ar, 1% CO in Ar, 1% NO + 1% CO in Ar.

Two kinds of oxide samples were studied: nickel manganite ($Ni_{0.70}Mn_{2.30}\square_{3\delta/4}O_{4+\delta}$) and nickel–copper manganite ($Ni_{0.22}Cu_{0.25}Mn_{2.53}O_{4+\delta}$). As a general trend, the spectra recorded for the adsorption of NO on nickel and nickel–copper manganites were very similar. However, the study of the surface species formed upon NO or CO adsorption on nickel–copper manganites was found to be more difficult than with nickel manganites due to the narrowing of the IR transparency window, leading to a decrease of the signal-to-noise ratio above 2000 cm^{-1}.

3.1 Static adsorption of NO on an outgassed surface ($T = -20\,°C$)

The adsorption of 1% NO/Ar was carried out at $-20\,°C$ in static conditions with an admission pressure of $P = 5 \times 10^4$ Pa. On nickel manganites (Fig. 1) the first spectrum, recorded at $t = 10$ s, showed the presence of a single absorption band at 1875 cm^{-1}. From $t = 17$ s, new bands appeared at 1920 cm^{-1} (as a shoulder to the previous band) and in the 900–1700 cm^{-1} region. These last bands progressively developed to give, from $t = 2$ min, five bands at 1535, 1375, 1280, 1190 and 1005 cm^{-1}. From $t = 4$ min, the intensity of the band at 1920 cm^{-1} decreased and a broad band appeared from $t = 10$ min at 2180 cm^{-1}. On the other hand, the bands observed in the 900–1700 cm^{-1} region also developed after $t = 4$ min to form three intense bands at 1535, 1250 and 1005 cm^{-1} and two weaker bands at 1635 and 1375 cm^{-1}.

Upon adsorption of 1%NO/Ar on nickel–copper manganites, two absorption bands were observed at 1880, 1925 cm^{-1} (Fig. 2). The position of these bands was very close to that of the bands observed for nickel manganites but, contrarily to the case of nickel manganites, the band at 1925 cm^{-1} was present from the very first spectra. The bands observed in the 800–1700 cm^{-1} region at 1635, 1600, 1375, 1255, 1180 and 990 cm^{-1} were quite similar to those observed in the case of nickel manganites.

When the sample was put back under vacuum and heated, the bands in the 1700–2500 cm^{-1} region progressively vanished as the temperature increased and no more bands were observed in this region above 100 °C. On the contrary, the intensity of the bands situated in the 900–1700 cm^{-1} region only slightly decreased below 100 °C, but they disappeared at higher temperatures (150–330 °C).

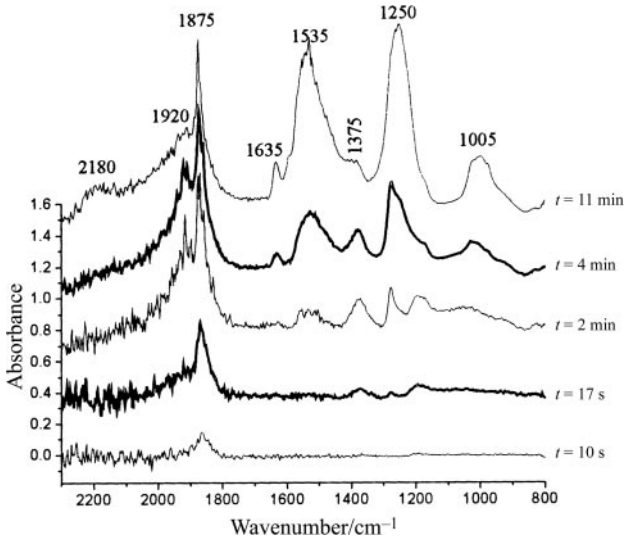


Fig. 1 Changes with time of FTIR spectra recorded on outgassed $Ni_{0.70}Mn_{2.30}O_{4+\delta}$ after static adsorption at $-20\,°C$ of 1%NO/Ar ($P = 5 \times 10^4$ Pa). Spectra are *y*-offset for clarity.

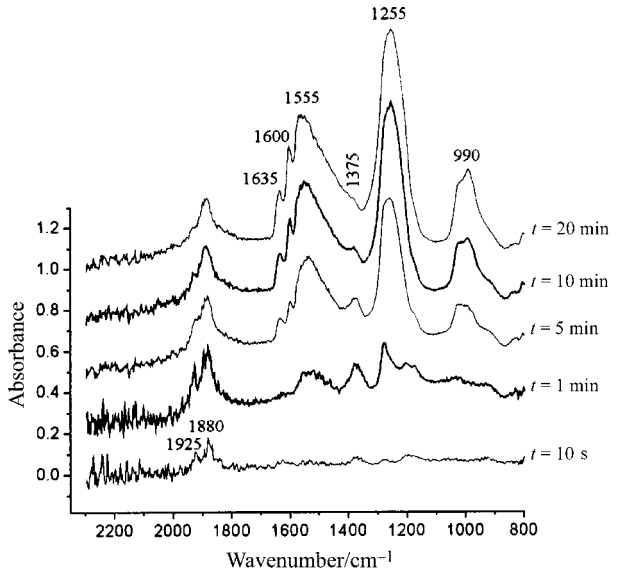


Fig. 2 Changes with time of FTIR spectra recorded on outgassed $Ni_{0.22}Cu_{0.25}Mn_{2.53}O_{4+\delta}$ after static adsorption at $-20\,°C$ of 1%NO/Ar ($P = 5 \times 10^4$ Pa). Spectra are *y*-offset for clarity.

3.2 Static adsorption of CO on an outgassed surface ($T = -20\,°C$)

The static adsorption of 1%CO/Ar was carried out at $-20\,°C$ with an admission pressure of 5×10^3 Pa to avoid saturation. From the very first seconds of contact between CO molecules and the surface of the sample, absorption bands were observed (Fig. 3) at 2340 cm^{-1} (strong), 2185/2195 cm^{-1} (doublet) and in the 1200–1700 cm^{-1} region at 1610, 1420, 1370, 1280 and 1220 cm^{-1}. The intensity of the 2185/2195 cm^{-1} doublet decreased progressively with time and merged into a single band at 2190 cm^{-1}.

When the sample was put back under vacuum, only the band at 2190 cm^{-1} quickly vanished, whereas the other bands remained. Heating was needed to recover the initial state of the surface. The band at 2340 cm^{-1} had completely disappeared at 25 °C, but a temperature of 320 °C was necessary to remove the bands in the 1200–1700 cm^{-1} region.

The adsorption of 1%CO/Ar on nickel–copper manganites (Fig. 4) gave bands in the 1200–1700 cm^{-1} region (at 1600, 1420, 1300 and 1210 cm^{-1}). As stated above, the decrease of the signal-to-noise ratio above 2000 cm^{-1} made investigations in this wavenumber region difficult. Nevertheless, absorptions at 2350 and 2130 cm^{-1} could be detected.

3.3 Static adsorption of the stoichiometric mixture NO + CO on an outgassed surface ($T = -20\,°C$)

Static adsorption of 1%NO + 1%CO + Ar was performed at $-20\,°C$ and $P = 5 \times 10^4$ Pa. The spectrum recorded after the admission of the gas mixture showed the presence of bands at

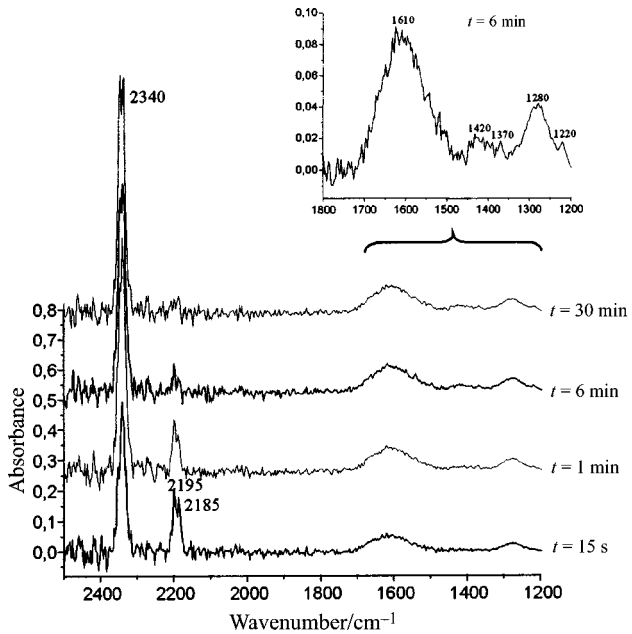


Fig. 3 Changes with time of FTIR spectra recorded on outgassed $Ni_{0.70}Mn_{2.30}O_{4+\delta}$ after static adsorption at $-20\,°C$ of 1%CO/Ar ($P = 5 \times 10^3$ Pa). Spectra are *y*-offset for clarity.

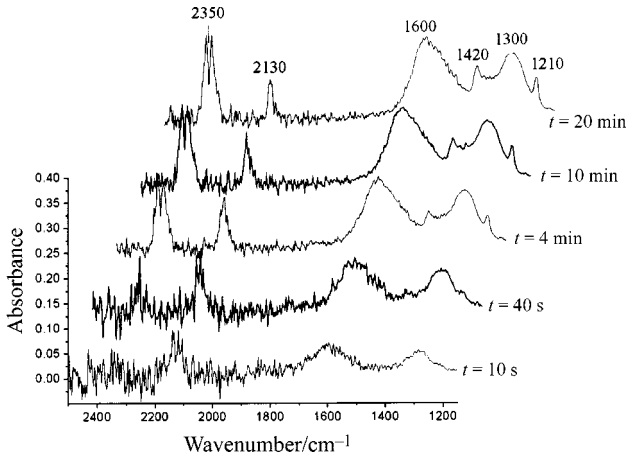


Fig. 4 Changes with time of FTIR spectra recorded on outgassed $Ni_{0.22}Cu_{0.25}Mn_{2.53}O_{4+\delta}$ after static adsorption at −20 °C of 1%CO/Ar ($P = 5 \times 10^3$ Pa). Spectra are *x* and *y*-offset for clarity.

2340, 2190, 1925 and 1875 cm^{-1} as well as a large group of bands at 1615, 1560, 1370, 1275 and 1190 cm^{-1}. A weak band was also observed at 2195 cm^{-1} just after contacting the gas mixture with the surface but this band disappeared rapidly from $t = 15$ s. The comparison with the 1%NO/Ar adsorption shows that, except for the band at 2340 cm^{-1} observed with NO + CO, there is a great similarity between both spectra recorded after 20 min of adsorption (Fig. 5).

3.4 Static adsorption of NO on a CO-preadsorbed surface ($T = -20$ °C)

This experiment was carried out to study the competitive adsorption behaviour between NO and CO. The CO preadsorption was carried out as described above (see Section 3.2). The remaining gas phase was then rapidly evacuated under primary vacuum and replaced by 1%NO/Ar (pressure: 5×10^4 Pa). From the first spectra recorded after introduction of the nitric oxide (Fig. 6), the bands at 1610, 1420, 1370, 1280 and 1220 cm^{-1} progressively disappeared whereas new bands appeared at 1870, 1920 and 2190 cm^{-1} and in the 900–1700 cm^{-1} region at 1630, 1540, 1380, 1255 and 1005 cm^{-1}. Moreover, the intensity of the band situated at 2340 cm^{-1} decreases notably from the admission of nitric oxide.

3.5 Static adsorption of CO on a NO-preadsorbed surface ($T = -20$ °C)

This experiment was symmetrical to the previous one. Except for the persisting presence of an absorption band at 2345

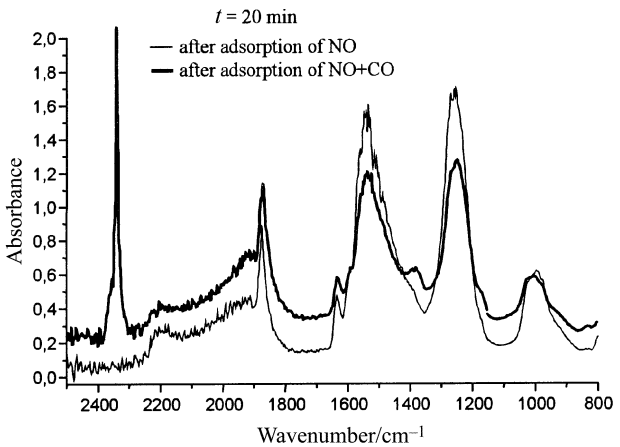


Fig. 5 Comparison of FTIR spectra recorded at $t = 20$ min on outgassed $Ni_{0.70}Mn_{2.30}O_{4+\delta}$ after static adsorption at −20 °C of 1%NO/Ar and 1%NO + 1%CO + Ar ($P = 5 \times 10^4$ Pa). Spectra are *y*-offset for clarity.

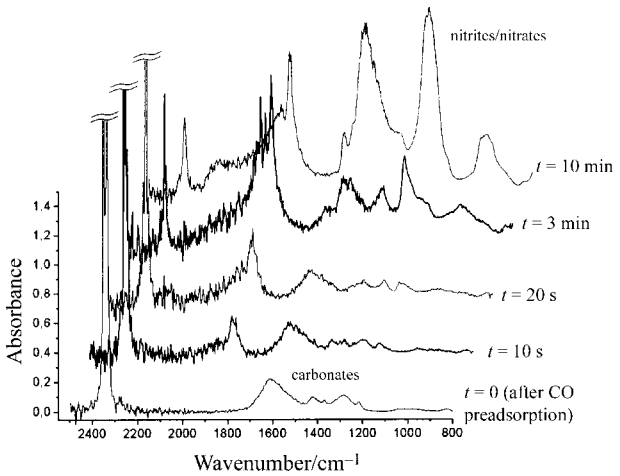


Fig. 6 Changes with time of FTIR spectra recorded on CO-preadsorbed $Ni_{0.70}Mn_{2.30}O_{4+\delta}$ after static adsorption at −20 °C of 1%NO/Ar ($P_{NO} = 5 \times 10^4$ Pa). Spectra are *x* and *y*-offset for clarity.

cm^{-1}, no modification could be observed compared to the case of NO adsorption on an outgassed surface.

3.6 Flowing adsorption of NO on an outgassed surface ($T = -20$ °C)

From the admission of the 1%NO/Ar flow (60 cm^3 min^{-1}) into the cell, bands appeared (Fig. 7) at 1865 cm^{-1} and in the 900–1700 cm^{-1} region at 1510, 1375, 1195 and 1055 cm^{-1} (the bands at 1375 and 1195 cm^{-1} being the strongest). With time on stream, new bands appeared at 1910 cm^{-1} and at 2210 cm^{-1} (from $t = 10$ min). The bands observed in the 900–1700 cm^{-1} region developed progressively into bands at 1600, 1525, 1385, 1275, 1195 and 1025 cm^{-1}.

When the sample was put back under pure argon (maintaining a flow of 60 cm^3 min^{-1}), the intensity of the band at 1865 cm^{-1} then the one at 1910 cm^{-1} quickly decreased. On the contrary, the bands in the 900–1700 cm^{-1} region were hardly altered.

3.7 Flowing adsorption of CO on an outgassed surface ($T = -20$ °C)

When the adsorption experiment was performed in a flow of 1%CO/Ar, no significant modification was observed compared with static adsorption. When putting the sample back

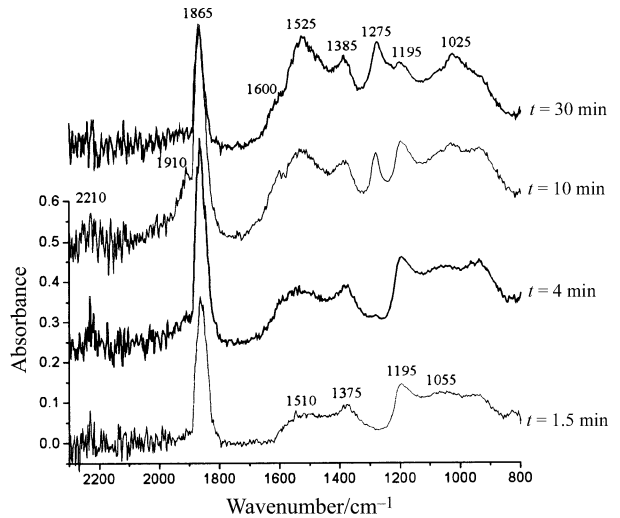


Fig. 7 Changes with time of FTIR spectra recorded on outgassed $Ni_{0.70}Mn_{2.30}O_{4+\delta}$ after flowing adsorption at −20 °C of 1%NO/Ar (P_{atm}, $f = 60$ cm^3 min^{-1}). Spectra are *y*-offset for clarity.

under pure argon, only the bands in the 1200–1700 cm^{-1} region persisted.

3.8 Flowing adsorption of the stoichiometric mixture NO + CO on an outgassed surface ($T = -20\,°C$)

The spectra recorded under flowing conditions for the adsorption of the stoichiometric gas mixture 1%NO + 1%CO + Ar were similar to those obtained in the case of NO flowing adsorption. In particular, no band was observed at 2340 cm^{-1}. Furthermore, no modification of the spectra was evidenced after switching to a flow of 1%CO/Ar.

4 Discussion

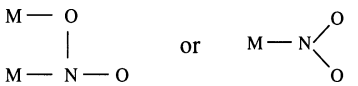
4.1 Adsorption of nitric oxide

The position of the band observed at 1870 cm^{-1} for nickel manganites (Fig. 1) and at 1880 cm^{-1} for nickel–copper manganites (Fig. 2) is very close to the vibration of gaseous nitric oxide molecule ($\bar{\nu}_{NO} = 1876\ cm^{-1}$). These bands can be attributed with no doubt[5] to *mononitrosyl* species and the closeness of their frequency to that of gaseous NO tends to show that the M–N bond involved in these species is rather weak.

Peña *et al.*[6] reported the formation of dinitrosyl species after NO adsorption on $LaMnO_3$, these species being detectable by the presence of a band at 1910 cm^{-1}. Hence, it may be assumed that the band observed in the present work at 1920 cm^{-1} for copper-free manganites (Fig. 1) and at 1925 cm^{-1} for nickel–copper manganites (Fig. 2) can also be assigned to *dinitrosyl* surface species. It can be noted that these species are formed faster for copper-containing samples, since the band at 1925 cm^{-1} is observed from the first seconds of adsorption of NO.

The bands observed in the 900–1700 cm^{-1} region after NO adsorption can be attributed to *nitrite/nitrate* species.[7–9] The free nitrate anion is planar and has a D_{3h} symmetry, hence it presents only one IR active mode (ν_{as}) at 1380 cm^{-1}. The respective ν_s is inactive in IR. But the surface nitrates usually have a C_{2v} symmetry, so that the ν_3 mode splits into 2 bands, $\nu_{as(NO_2)}$ and $\nu_{s(NO_2)}$, and the ν_1 mode becomes IR active. Hence the bands observed at 1640–1530, 1250–1280 and 1005 cm^{-1} could be assigned respectively to ν_{as}, ν_s and ν_1 of mono- or bidentate nitrates.

On the other hand, bands at 1375 and 1190 cm^{-1} could be related to nitrites involving an M–N bond as in:[10]



With time, the intensity of the band attributed to dinitrosyl species decreases and a new band appears at 2180 cm^{-1} for nickel manganites (Fig. 1). The presence of a band in the 2200–2290 cm^{-1} region has already been reported by numerous authors[11–15] and has been attributed to the N–N stretching vibration in adsorbed N_2O (the N–O modes are generally not identifiable because of the strong bands due to the substrate[9]). Moreover, a study by temperature programmed desorption of nitric oxide on nickel and nickel–copper manganites[3] has shown that part of the nitric oxide (10 to 30%) desorbed as nitrous oxide. The late appearance of this species and the decrease of the intensity of the band related to dinitrosyl species tend to show that nitrous oxide originates from the partial decomposition of dinitrosyl species, such as:

$$M\text{–}(NO)_2 + \text{vacant site} \rightarrow M\text{–}N_2O + O_{(ads)}$$

It can be noted that the most intense bands observed in the 1200–1700 cm^{-1} region are mainly due to nitrite species for the first spectra, and to nitrates from $t \approx 4$ min (Fig. 1 and 2). A possible evolution from nitrites to nitrates (oxidation process) could thus be assumed. In order to shed some light on this point, oxygen was admitted to the cell after pre-adsorption of NO and evacuation under primary vacuum of the remaining gas phase. The resulting IR spectra (Fig. 8) show that the intensity of the bands related to nitrate species strongly increases in the presence of oxygen, whereas that of the bands attributed to nitrites and nitrosyls decreases. This experiment tends thus to indicate that nitrates could arise from the oxidation of nitrite species, the latter most probably originating from the oxidation of nitrosyl species. This would also explain that nitrosyl species were the first to be observed at $t = 10$ s upon NO adsorption (see Fig. 1 and 2).

The bands corresponding to mononitrosyls, dinitrosyls and adsorbed N_2O disappear below 100 °C upon heating under vacuum, pointing out the low stability of these surface species. On the contrary, the persistence at higher temperatures of the bands observed in the 900–1700 cm^{-1} region shows that nitrites and nitrates are far more stable species.

When NO adsorption is carried out under flowing conditions (Fig. 7), similar species can be identified as in the case of static adsorption. However, one can note a higher relative intensity of nitrites compared to nitrates than for static conditions. If a flow switch "1%NO/Ar → Ar" is performed, the bands relating to nitrosyls and adsorbed nitrous oxide rapidly disappear, whereas bands due to nitrites and nitrates hardly change. Again, this underlines the high stability of nitrites and nitrates.

Comparison between NO adsorption on nickel and nickel–copper manganites (Fig. 1 and 2) shows that similar bands are observed in both cases. Notwithstanding, for copper-containing oxides, fewer nitrosyl species are observed and dinitrosyl species are formed faster.

4.2 Adsorption of carbon monoxide

In all cases, the adsorption of CO on nickel or nickel–copper manganites led to the formation of a band at 2340–2350 cm^{-1} (Fig. 3 and 4). The position of this band is very similar to the ν_3 vibration of the CO_2 molecule ($\nu_3(CO_2) = 2349\ cm^{-1}$) and this band can thus be linked to carbon dioxide. Furthermore, the presence of a unique branch (not a doublet) clearly visible for nickel manganites (Fig. 3) shows that the band at 2340 cm^{-1} may be assigned to *chemisorbed* CO_2. The persistence of this band under vacuum also confirms that it is due to chemically bound CO_2 rather than gaseous CO_2. Hence, even at low temperature, CO could react with the surface oxygen of the oxide to form CO_2. Indeed, under flowing 1%CO/Ar gas mixture, the presence of CO_2 was evidenced in the outlet gas, indicating a surface reduction.

Upon CO adsorption, IR bands were also observed at 2180–2195 cm^{-1} for nickel manganites (Fig. 3) and at 2130

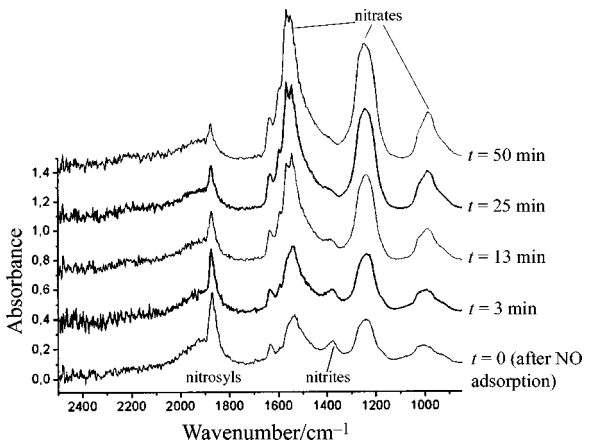


Fig. 8 Changes with time of FTIR spectra recorded on NO-preadsorbed $Ni_{0.70}Mn_{2.30}O_{4+\delta}$ after introduction at −20 °C of pure O_2 ($P_{O_2} = 5 \times 10^4$ Pa). Spectra are *y*-offset for clarity.

cm^{-1} for nickel–copper manganites (Fig. 4). The position of these bands is close to the vibration of gaseous carbon monoxide molecule ($\bar{\nu}_{CO} = 2143\ cm^{-1}$) and these bands can thus be attributed to *carbonyl* species. The fast disappearance of these bands with time or under vacuum indicates that these species present a low stability.

The bands observed after CO adsorption in the 1200–1700 cm^{-1} region (Fig. 3 and 4) can be attributed to monodentate or bidentate *carbonates*.[8] These species are particularly stable as shown by the persistence of the corresponding bands below 300 °C under vacuum.

4.3 Competitive adsorption between NO and CO

When the adsorption of nitric oxide is carried out on a CO-preadsorbed surface (Fig. 6) the bands corresponding to carbonate species are quickly replaced by new bands at 1630, 1540, 1380, 1255 and 1005 cm^{-1} that are attributable as above to nitrite/nitrate species. On the other hand, the intensity of the band situated at 2340 cm^{-1}, due to chemisorbed CO_2, decreases notably while new bands appear at 1870 (mononitrosyls), 1920 (dinitrosyls) and 2190 cm^{-1} (adsorbed N_2O). These results confirm that NO is able to displace CO preadsorbed molecules, as was already shown from chemisorption experiments.[2]

If the adsorption of carbon monoxide was carried out on a NO-preadsorbed surface, no modification was observed, except for the formation of a band at 2345 cm^{-1} corresponding to chemisorbed CO_2. This point shows that CO is not able to displace NO-preadsorbed molecules, here again in accordance with the chemisorption results.[2] In the case of copper-containing samples, a band at 2135 cm^{-1} was observed during the first seconds after introduction of CO in the cell. The position of this band indicates the formation (furtive) of carbonyl species, most probably involving copper cations as this band is not detected for copper-free manganites. Indeed, Davydov[8] reported the observation at 2130 cm^{-1} of a band assigned to Cu^+–CO carbonyl species formed on the surface of copper oxide.

The adsorption experiments carried out with the stoichiometric gas mixture 1%NO + 1%CO + Ar (Fig. 5) also showed that NO covers the surface of the sample at the expense of carbon monoxide, since the spectra recorded at $t = 20$ min after adsorption of NO and NO + CO are rather similar (except for chemisorbed CO_2).

5 Conclusions

This work reports an *in situ* FTIR analysis of the surface species formed upon adsorption of nitric oxide and carbon monoxide on nonstoichiometric nickel and nickel–copper manganites. As a general trend, the spectra recorded with copper-containing and copper-free samples were very similar. The adsorption of nitric oxide led to the formation of nitrites/nitrates, mononitrosyl and dinitrosyl species. Nitrates are thought to originate from partial oxidation of nitrites, themselves arising from oxidation of nitrosyl species. On the other hand, at least with nickel manganites, dinitrosyl species progressively decomposed to give adsorbed N_2O and oxygen adatoms. The dinitrosyl species formed with copper-containing manganites appeared faster than for nickel manganites but were less numerous. This could be accounted for by a lower stability of the dinitrosyl species involving copper.

Upon adsorption of carbon monoxide, carbonyl and carbonate species were evidenced as well as chemisorbed CO_2. The carbonyls were found to be quite unstable, whereas carbonates only decomposed above 300 °C.

The study of the competitive adsorption behaviour of NO and CO on these oxides indicated that, in accordance with previous results, NO presented the tendency to colonize the surface, being able to displace CO preadsorbed molecules. However, for copper-containing samples, the appearance of an absorption band at 2135 cm^{-1} (most probably related to Cu^+–CO carbonyls) when carbon monoxide is contacted with a NO-preadsorbed surface tends to show that cuprous cations may be the unique access points of CO to the surface of such oxides in the presence of NO.

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